



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



⑪ Publication number:

**0 533 073 A1**

## EUROPEAN PATENT APPLICATION

) Application number: 92115614.7

⑤① Int. Cl.<sup>5</sup>: G21C 3/07

) Date of filing: 11.09.92

) Priority: 16.09.91 US 760648

) Date of publication of application:  
24.03.93 Bulletin 93/12

) Designated Contracting States:  
BE CH DE ES FR GB IT LI SE

⑦① Applicant: Siemens Power Corporation  
2101 Horn Rapids Road  
Richland, WA 99352(US)

⑦② Inventor: Van Swam, Leo F.P.  
1974 Forest Avenue  
Richland, WA 99352(US)  
Inventor: Busch, Raymond A.  
Rt. 2, Box 2289  
Richland, WA 99352(US)

⑦④ Representative: Fuchs, Franz-Josef, Dr.-Ing.  
Postfach 22 13 17  
W-8000 München 22 (DE)

) Structural elements for a nuclear reactor fuel assembly.

⑦ A structural element for use in a nuclear reactor fuel assembly has an inner layer composed of a high strength zirconium alloy and an outer layer covering the inner layer with the outer layer composed of a highly corrosion and hydrogen absorption and permeation resistant zirconium alloy. The inner and outer layers are metallurgically bonded continuously over their contacted surfaces to produce an integral structure. The inner layer comprises from 50-92% of the finished structural element. Preferably the inner layer is Zircaloy-2 or -4. The outer layer comprises the balance of the structural thickness and is preferably a zirconium-tin-iron alloy or a zirconium-niobium alloy. The outer zirconium alloy layers cover the inner layer to limit exposure of the inner layer to the aggressive cooling environment encountered in a nuclear reactor. By combining these layers into a unitary structure, a structural element having superior strength and creep properties is provided which has enhanced corrosion and hydrogen absorption resistance.

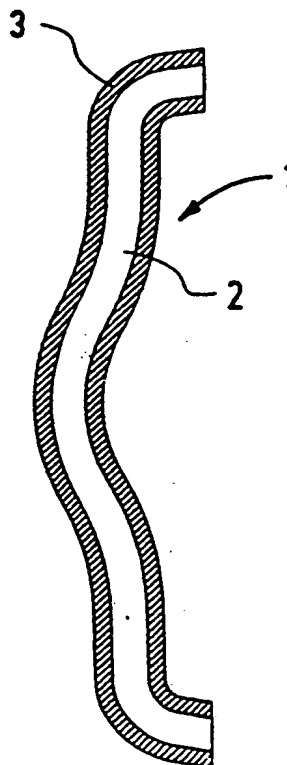


FIG 1

## TECHNICAL FIELD

This invention relates to structural elements for nuclear reactors and more particularly to highly corrosion resistant structural elements for use in a nuclear reactor fuel assembly.

## BACKGROUND

Structural elements for nuclear fuel assemblies must be capable of surviving in an extremely harsh environment. These elements may include spacer grids and side plates, structural channels, water rods, water rods, guidetubes and possibly fittings and fastening devices. For example, a spacer grid maintains a plurality of fuel rods incorporated in a nuclear fuel assembly in an organized array. These structures must maintain their strength in a highly radioactive environment and be resistant to corrosion by the coolant circulating around the fuel rods at high temperature. Since these structures are in continuous contact with a coolant such as water and/or steam with, at times, small amounts of impurities such as boric acid, lithium hydroxide, and other impurities, they are subject to severe corrosion stresses from oxidation at high temperature. Dissolved hydrogen may be present in the coolant, which may permeate into and react with the alloys forming the structures and cause weakening through embrittlement and/or by increasing the propensity for corrosion.

To reduce radioactive waste generation and increase efficiency, there is an increasing trend to design fuel assemblies which have a longer burn-life. To achieve this, the structural elements will be required to endure the harsh aqueous environment for longer periods of reactor operation, accordingly requiring the retention of their structural and corrosion resistant properties for those extended periods.

To meet these requirements, zirconium alloys are typically used in forming the structural elements for nuclear fuel assemblies. However, while some zirconium alloys have high strength, they are also susceptible to high corrosion rates in an aqueous environment. Other zirconium alloys which are more corrosion resistant may not meet mechanical strength requirements. To date, these structures have typically been made of alloys, such as Zircaloy-2 or -4. Stainless steel and Inconel alloys have also been used, but these materials suffer from a high neutron capture cross section and therefore, are detrimental to high efficiency operation of the assemblies.

In U.S. Patent No. 4,751,044, a nuclear fuel cladding tube is described having two annular layers bonded to each other. An inner layer is composed of a zirconium base alloy and an outer layer

is composed of a titanium base material which protects the zirconium from the corrosive environment of the reactor core coolant.

In U.S. Patent No. 3,620,691 a fuel rod structure is disclosed having a high strength zirconium inner layer, a gas diffusion-impeding material on the surface thereof and a highly corrosion-resistant zirconium layer surrounding the gas impeding layer.

Other fuel rod structures are disclosed in U.S. Patent Nos. 5,023,048, 4,675,153, 4,863,679, 4,610,842, 4,963,316 and 4,735,768. However, fuel rod cladding structures require application specific properties, since they are used to contain nuclear fuel pellets. Thus, fuel rods experience different environments on the inner and outer surfaces and do not serve the same purpose as structural elements in a nuclear reactor.

## SUMMARY OF INVENTION

It is an object of the present invention to provide a structural element which has enhanced corrosion resistance and high mechanical and creep strength for use in a nuclear reactor.

It is another object to provide a structural element for use in a nuclear fuel assembly which is resistant to hydrogen absorption.

These and other objects of the present invention are achieved by providing a structural element for a nuclear fuel assembly comprising an inner layer composed of a high strength and creep resistant zirconium base alloy and outer layers covering the inner sheet, the outer layers composed of a corrosion resistant and hydrogen absorption resistant zirconium base alloy.

The inner layer and outer layers are metallurgically bonded continuously over their surfaces to assure integrity at the interface. Preferably, these layers are roll bonded or diffusion bonded into a unitary structure prior to fabrication into a structural element.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a structural element of the present invention in cross section.

Fig. 2 shows a composite plate or sheet of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1, a strip 1 has an inner layer 2 and an outer layer 3. The strip may be used in various structural elements of a nuclear fuel assembly, such as to provide a spacer strip which is used to maintain a plurality of nuclear fuel rod assemblies in an organized array. As such, due to its

proximity to the nuclear fuel rods and the need to maintain an organized array under even extreme conditions to assure adequate cooling, the strip must have adequate mechanical strength and adequate creep properties. In addition, the strip must maintain these properties in a hot aqueous environment for extended periods of operation. Thus, long term resistance to corrosion, to hydrogen embrittlement and to neutron radiation is required.

The inner layer could be a zirconium base alloy such as Zircaloy-2 or -4. Such a material provides sufficient strength to survive under standard operating or accident conditions. The outer layers are preferably composed of a zirconium alloy which has higher corrosion resistance as compared to Zircaloy-2 or -4 and increased resistance to hydrogen absorption. Such a composite layer has the advantage of being easily formable into a structural element such as a channel or spacer strip. It can also be fabricated by welding into other structures without causing significant exposure of the inner sheet, as the corrosion resistant zirconium layer continues to cover the high strength inner layer. For purposes of this disclosure, the terms zirconium and zirconium alloy includes such small amounts of impurities which are typically encountered.

Referring again to Fig. 1, the inner layer 2 is formed of Zircaloy-2 or -4. Zircaloy-2 contains 1.2-1.7% by weight tin, 0.07-0.2% iron, 0.05-0.15% chromium, 0.03-0.8% nickel, 0.07-0.15% oxygen and balance zirconium and incidental impurities. Zircaloy-4 contains 1.2-1.7% tin, 0.18-0.24% iron, 0.7-0.13% chromium, 0.1-0.16% oxygen and the balance zirconium and incidental impurities. Other alloys useable as the inner layer are zirconium alloys with about 0-2% tin, 0-10% niobium, 0-0.5% Fe, 0-0.2% Cr, 0-0.2% Ni, 0.05-0.20% oxygen and small amounts of impurities as may typically be encountered in nuclear grade zirconium sponge. Impurities within the normal range for commercial reactor grade sponge zirconium are Aluminum 75 ppm or less, Boron 0.5 ppm or less, Cadmium 0.5 ppm or less, Carbon 270 ppm or less, Chromium 200 ppm or less, Cobalt 20 ppm or less, Copper 50 ppm or less, Hafnium 100 ppm or less, Iron 1500 ppm or less, Hydrogen 25 ppm or less, Oxygen 900 ppm or less, Magnesium 20 ppm or less, Manganese 50 ppm or less, Molybdenum 50 ppm or less, Nickel 70 ppm or less, Nitrogen 65 ppm or less, Silicon 120 ppm or less, Tin 50 ppm or less, Titanium 50 ppm or less, Tungsten 100 ppm or less, and Uranium (total) 3.5 ppm or less. Of course, other zirconium base alloys having the desired structural properties could be used.

The strip outer layer 3 is formed of a corrosion resistant zirconium alloy. For example, about 0.5% tin, 0.4% iron, balance zirconium and incidental

impurities, or about 0.8% tin, 0.2% iron, 0.1% chromium, balance zirconium and incidental impurities; or about a 0.5% tin, 0.2% iron, 0.1% chromium, balance zirconium alloy and incidental impurities could be used. Other alloys usable include a zirconium-niobium alloy such as zirconium with about 0.5-3% niobium or zirconium alloys having about 0-3% niobium, 0-1.0% tin, 0-0.5% iron, 0-0.3% chromium, 0-0.3% nickel, 0.05-0.20% oxygen, and the balance zirconium and incidental impurities.

Zirconium alloys that resemble the composition of Zircaloy-2 or -4, but which have a much lower tin concentration (below approximately 1% tin by weight) are preferred as they have shown very good corrosion resistance in pressurized water reactor environments. The good corrosion resistance also leads to very low hydrogen pick-up levels. Alloys containing niobium are also preferred as they have shown increased resistance to modular corrosion frequently observed in water cooled reactors.

The inner layer 2, constructed of either Zircaloy-2 or -4, or other compositions as indicated above, are bonded to the outer layers 3 composed of the corrosion resistant alloy. Various types of metallurgical bonding processes may be used such as rolling, extrusion, hot pressing, explosive bonding or diffusion bonding. The sheets are bonded continuously over their surfaces.

Referring to Fig. 2, a plate 4 is fabricated by placing a first outer sheet 5, an inner sheet 6 and a second outer sheet 7 together as a stack. The edges of the stack are then welded together to bond the outer sheets together to prevent oxidation in between the layers during bonding. The stack is then heated and rolled in a conventional rolling mill to bond the sheets together into an integral structural plate or sheet.

The relative thicknesses of the sheet 6 to the sheets 5 and 7 may be, for example, about 80% to 10% to 10%, respectively. From about 4-25% of the overall sheet thickness could be comprised of each of the outer sheets (balance, about 50-92% being the inner sheet). While the outer sheets may be of equal thickness, they need not be, and depending on the exposure of the surface, a relatively thicker sheet could be put on one side of the central sheet and a thin sheet on the other side. For example, if one side of the structural element will experience, in addition to coolant contact, significant wear, a relatively thicker surface sheet is provided on this side for prolonged corrosion protection. Typically outer sheets 5 and 7 would be of the same alloy composition although there may be instances where dissimilar alloys are favored.

When used as a spacer strip for supporting a plurality of fuel rods for a nuclear fuel assembly,

0 → 10%  
3% Nb  
all imp. ≠  
→ as a  
n'importe  
pour elle  
laquelle  
↓  
decision  
OEB?  
by box

inner layer has a thickness of about 0.005 to 0 inch to provide sufficient structural strength to withstand the mechanical forces which could be encountered. This inner layer is essentially not exposed to contact with the coolant fluid, since the inner sheet is nearly continuous thereover.

At the edges of the strip, the surface area of inner layer exposed to the coolant is very small, and since the inner layer has at least moderate resistance to corrosion, the overall corrosion of the strip and the hydrogen absorption rate are only minimally affected.

While in the preferred embodiments of the present invention, a spacer strip is described, it will be understood by those skilled in the art that various other structural elements usable in a nuclear reactor may be produced according to the present invention. Consequently, various changes and modifications could be made by those skilled in the art without varying from the scope of the present invention.

#### Claims

A structural element for use in a nuclear reactor comprising an inner layer composed of a high strength zirconium alloy and outer layers covering the inner layer, the outer layers composed of a highly corrosion and hydrogen absorption and permeation resistant zirconium alloy, the inner layer and the outer layers metallurgically bonded continuously over their contacted surfaces to produce an integral structural element.

The element of claim 1 wherein the inner layer is a Zirconium alloy comprising 1.2-1.7% by weight tin, 0.07-0.2% iron, 0.05-0.15% chromium, 0.03-0.8% nickel, 0.07-0.15% oxygen, 0-0.012% silicon, and 0-0.027% carbon.

The element of claim 1 wherein the inner layer is a Zirconium alloy comprising 1.2-1.7% tin, 0.18-0.24% iron, 0.07-0.13% chromium, 0.1-0.16% oxygen, 0-0.012% silicon, and 0-0.027% carbon.

The element of claim 1 wherein the inner layer is a zirconium alloy with about 0-2% tin and 0-10% niobium.

The element of claim 1 wherein the outer layer comprises a zirconium alloy having about 0.1 - 1.0% tin, 0.1 - 0.5% iron.

The element of claim 1 wherein the outer layer comprises a zirconium alloy having about 0.1 - 1.0% tin, 0.05 - 0.5% iron, 0.02 - 0.2% chro-

mium.

- 5 7. The element of claim 1 wherein the outer layer comprises a zirconium alloy having about 0.1 - 1.0% tin, 0.05 - 0.2% chromium.
- 10 8. The element of claim 1 wherein the outer layer comprises a zirconium alloy having about 0.1 - 1.0% tin, 0.05 - 0.5% iron, 0.01 - 0.20% nickel.
- 15 9. The element of claim 1 wherein the outer layer is a zirconium alloy containing about 1.0-3.0% niobium.
- 20 10. The element of claim 1 wherein the outer layer comprises a zirconium alloy having about 1.0-3.0% niobium, 0-1% tin, 0-0.5% iron, 0-0.3% chromium, 0-0.3% nickel.
- 25 11. The element of claim 1 wherein the inner and outer layers are metallurgically bonded by hot rolling.
- 30 12. The element of claim 1 wherein the inner layer comprises from about 50-92% of the overall thickness of the element.
- 35 13. The element of claim 1 wherein the inner layer comprises about 80% of the overall thickness of the element.
- 40 14. The element of claim 1 wherein the inner and outer layers are metallurgically bonded by a process selected from the group consisting of rolling, extrusion, hot pressing, explosive bonding and diffusion bonding.
- 45 15. The element of claim 1 wherein the outer layer is a zirconium alloy containing less than about 1% tin.
- 50
- 55

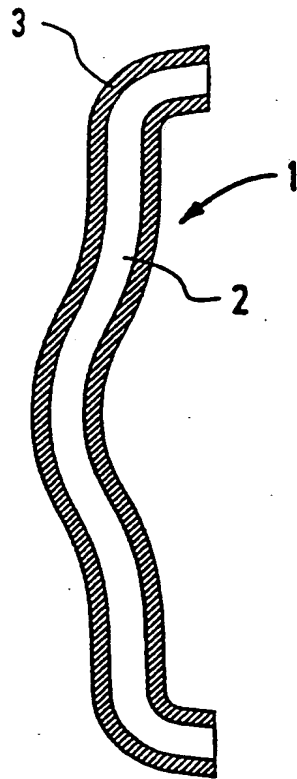


FIG 1

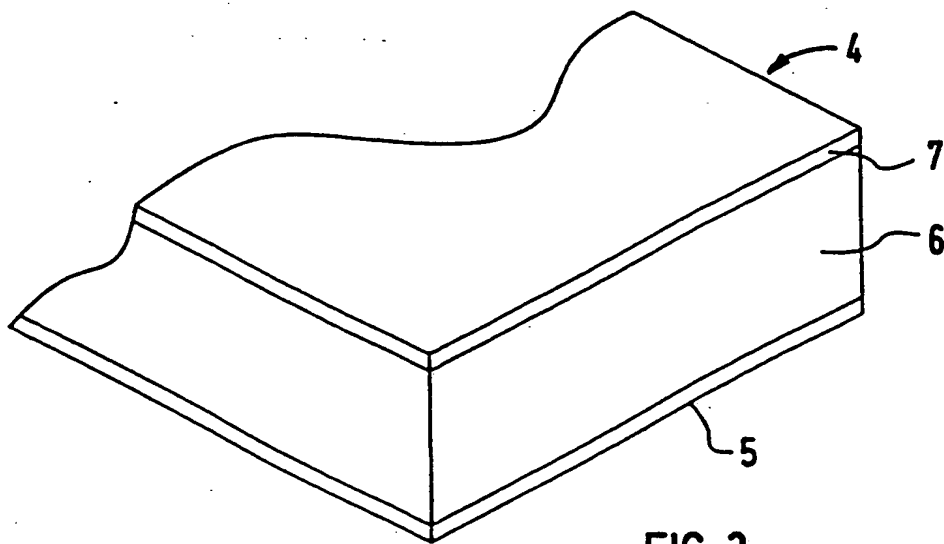


FIG 2



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 11 5614

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CLS)
	EP-A-0 353 733 (HITACHI) * page 3, line 27 - line 42; claims 1-26 *	1,11 2-10, 12-15	G21C3/07
	EP-A-0 154 559 (HITACHI) * claims 1,5-6,10,15; figures 2-3 *	1,11 2-10, 12-15	
	PATENT ABSTRACTS OF JAPAN vol. 9, no. 171 (C-291)16 July 1985 & JP-A-60 043 450 ( HITACHI ) 8 March 1985 * abstract *	1-10, 14-15	
	PATENT ABSTRACTS OF JAPAN vol. 10, no. 182 (C-356)(2238) 25 June 1986 & JP-A-61 030 681 ( HITACHI ) 12 February 1986 * abstract *	1-10,15	
A	US-A-4 751 044 (HWANG ET AL.) * claims 1-14 *	1-15	TECHNICAL FIELDS SEARCHED (Int. CLS)
A	US-A-3 620 691 (RUBEL) * claims 1-5 *	1-15	G21C

The present search report has been drawn up for all claims

Place of search

THE HAGUE

Date of completion of the search

17 DECEMBER 1992

Examiner

DEROUBAIX P.G

#### CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone  
Y : particularly relevant if combined with another document of the same category  
A : technological background  
O : non-written disclosure  
P : intermediate document

T : theory or principle underlying the invention  
E : earlier patent document, but published on, or after the filing date  
D : document cited in the application  
L : document cited for other reasons

A : member of the same patent family, corresponding document